



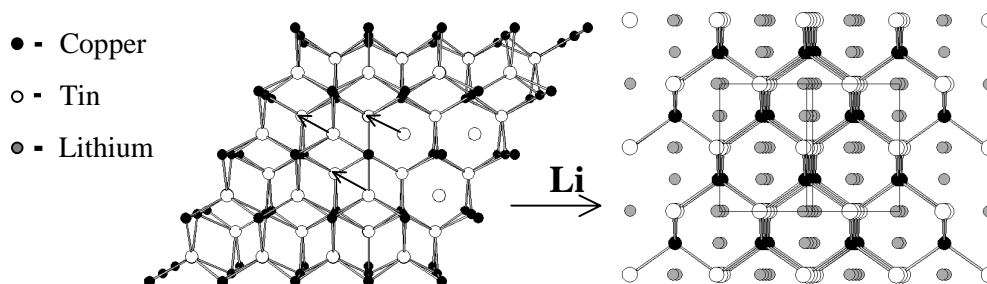
Development of Advanced Electrode Materials for Lithium-Ion Batteries

Lithium-ion batteries are being developed and manufactured worldwide for powering electronic devices such as cellular phones and laptop computers and for electric and hybrid vehicles. State-of-the-art lithium-ion batteries use lithiated graphite (LiC_6) negative electrodes coupled to LiCoO_2 positive electrodes via an organic electrolyte. These 4-V batteries are inherently unsafe and require sophisticated electronic circuitry to protect individual cells from being overcharged when the potential of the lithiated graphite electrode reaches that of metallic lithium, and when the LiCoO_2 electrode is extensively delithiated. A need, therefore, exists for alternative electrode materials that reduce the safety hazards as well as improve the performance.

Research at CMT on alternative negative electrode materials to graphite has focused on a new class of intermetallic materials with NiAs- and zinc-blende-type structures. These materials react electrochemically with lithium at a few hundred millivolts above the potential of metallic lithium.

In particular, we discovered that a Cu_6Sn_5 electrode (NiAs-type structure) undergoes a topotactic phase transition at ~ 400 mV (vs. lithium) to yield Li_2CuSn ,

in which the CuSn component has a zinc-blende arrangement of atoms (as shown in the figure). Further lithiation of Li_2CuSn results in an expulsion of metallic Cu from the structure and the formation of $\text{Li}_{4.4}\text{Sn}$. Unfortunately, although this reaction is reversible, capacity is lost steadily from the copper-tin electrode during charge and discharge. The capacity loss is attributed to grain growth of the extruded copper, electrode expansion, and loss of contact of the copper with the lithiated Sn particles. We have found that this problem can be minimized when the cycling is limited to the topotactic reaction. In this case, the copper-tin electrode will attain a rechargeable gravimetric capacity of ~ 200 mAh/g, which translates to a volumetric capacity of 1040 mAh/mL based on the density of Li_2CuSn (5.2 g/mL). Although the gravimetric capacity of the copper-tin electrode is inferior to that of lithiated graphite (theoretical value of 372 mAh/g), the practical volumetric capacity exceeds the theoretical value of lithiated graphite (818 mAh/mL). As a result, copper-tin electrodes are attractive for lithium-ion battery applications when volume is a more important consideration than mass.



Structural Schematic Representing the Cu_6Sn_5 to Li_2CuSn Transformation

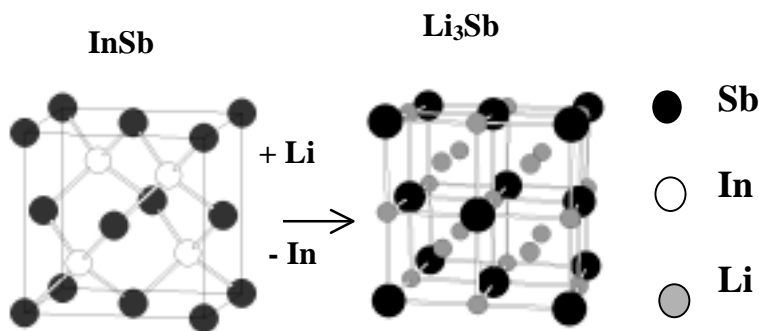
Our research on intermetallic electrode materials with a zinc-blende-type structure has focused on the family of antimony-based semiconductors, of which InSb has yielded the most promising results. We determined that the electrochemical reaction with lithium takes place by lithium insertion and indium extrusion from a stable face-centered-cubic Sb array between 900 and 600 mV (vs. lithium), yielding Li_3Sb on complete extrusion of indium (see figure). What is remarkable about the reaction is that the Sb array expands by only 4.4% during lithiation, and that after one conditioning cycle, the reaction is reversible. Further capacity can be obtained from the electrode if lithiation of the extruded In is allowed to take place (<600 mV vs. lithium). We found that InSb electrodes offer a practical rechargeable gravimetric capacity of ~300 mAh/g, which is equivalent to a volumetric capacity of 1290 mAh/mL, based on the average density of the

InSb electrode after reaction with lithium to form Li_3Sb and In (4.3 g/mL). These results hold great promise for developing an alternative electrode that is safe and able to endure many cycles without capacity decline.

The research on intermetallic electrodes has been sponsored primarily by DOE's Office of Basic Energy Sciences and Office of Advanced Automotive Technologies. This research has led to a Work-for-Others contract with an industrial firm.

ANL Participants

Michael M. Thackeray, Christopher S. Johnson, John T. Vaughey, Arthur J. Kahaian, Roy Benedek, Jeremy A. Kropf, and Holger C. Tostmann. For further information contact Michael Thackeray at (630) 252-9184 or thackeray@cmt.anl.gov.



Schematic of Structural Relationship between InSb and Li_3Sb